Multiphase Photocatalytic Oxidation in a Microreactor

Yoshihisa Matsushita,*[1] Mayuko Iwasawa,[2] Tadashi Suzuki,[3] and Teijiro Ichimura[3]
[1]*Department of Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8551*
[2]*Department of Applied Chemistry, Tokyo University of Agriculture and Technology,*
Naka-cho, Koganei, Tokyo 184-8588
[3]*Department of Chemistry and Materials Science, Tokyo Institute of Technology,*
Ookayama, Meguro-ku, Tokyo 152-8551

(Received June 2, 2009; CL-090532; E-mail: matsushita.y.aa@m.titech.ac.jp)

Photocatalytic oxidation of *p*-chlorophenol and toluene under gas–liquid–solid multiphase flow conditions was investigated by using a photocatalytic microreaction system. By loading both gaseous and liquid samples simultaneously into a microchannel with a photocatalytic titanium dioxide thin layer therein, a gas–liquid–solid multiphase annular flow was generated. The reaction yield was greatly enhanced with decreasing thickness of liquid layer because of improved efficiency of interaction and mass transfer between different phases.

Over the past decade, microreaction systems have attracted increasing attention in chemistry and demonstrated significant promise in a wide range of chemical transformations utilizing features unique to microspace.[1,2] In particular, microreaction systems show potential for use in catalytic reactions because of their large surface to volume ratio. Among research of catalytic reactions in microreaction systems, several examples have been reported to date on photocatalytic degradation of environmental pollutants in microreactors with immobilized titanium dioxide (TiO_2).[3–5] However the application of microreactors to photocatalytic reactions has not been subject to systematic research. Thus we developed a microreaction system optimized for photocatalytic reactions and investigated photocatalytic oxidation, reduction, and alkylation processes in a photocatalytic microreaction system.[6–10]

We further investigated oxidation processes of *p*-chlorophenol and toluene by using a multiphase flow formed in the photocatalytic microreaction system. Though numerous attempts at multiphase catalytic reactions in macroscale batch reaction vessels have been made, there are still difficulties in conducting the reactions due to low yield caused by very low efficiency of interaction and mass transfer between different phases.[11] Flows in microchannels are laminar with Reynolds numbers of less than several hundred. The continuous flow without turbulence in a microchannel helps to sustain an ordered structure. One can expect to employ interfaces between multiple phases in the microchannel flow for effective reaction and separation of reaction products. It is conceivable that the reaction efficiency can be improved by an application of triple phase flow where a flow is formed by constant contact of three phases, gas, liquid, and solid catalyst.[12] To produce high interfacial area between the phases and achieve efficient multiphase photocatalytic reactions, we introduced aqueous solutions of *p*-chlorophenol or methanol solutions of toluene and oxygen gas simultaneously into a microchannel with immobilized solid photocatalyst. The effect of the multiphase flow conditions on the photocatalytic oxidation was examined.

Photooxidation was carried out with a microreactor made of quartz which has a straight microchannel of 40 mm in length. The microchannel has a rectangular cross section of 500 μm in width and depth, and the bottom and side walls of the microchannel were coated with a photocatalytic TiO_2 layer by sol–gel method. To take advantage of the miniaturized reaction vessel, a light source of minimal space and low photon cost is suitable for the microreaction system. Thus we employed an array of 365-nm light-emitting diodes (UV-LEDs, Nichia NSHU590B ×7, total optical power output: 9.8 mW) for the excitation light source of photocatalyst instead of conventional UV lamps. Aqueous solutions of *p*-chlorophenol (1.0 mM) or methanol solutions of toluene (1.0 mM) were employed as a substrate for photocatalytic oxidation. Oxygen, nitrogen, or air was introduced into the microchannel simultaneously with the solution to form multiphase flow conditions and then irradiated with the array of UV-LEDs. It was confirmed that there was no significant change in photocatalytic activity of the immobilized TiO_2 layer after more than 24-h irradiation of the UV-LEDs under typical experimental conditions. Though formation of some intermediates was reported in photocatalytic oxidation of *p*-chlorophenol and toluene in batch reaction vessels,[13] only trace amount of these intermediate was detected probably resulting from fast successive degradation in the microreactor. Thus the yield of photooxidation was determined by monitoring concentration change of the substrates by gas chromatography. All experiments were carried out at room temperature.

The sample solution was injected into the microchannel at a constant flow rate while changing the injection rate of the gas phase. At a relatively low gas flow rate, alternate slug flow of the liquid and gas were observed. At a gas injection rate higher than 300 μL min^{-1}, an annular flow, with gas flowing through the center of the microchannel while a thin layer of the liquid flowed in the vicinity of the photocatalyst surface, was formed as schematically illustrated in Figure 1.

The photooxidation yield of *p*-chlorophenol in aqueous solution is shown in Figure 2. The horizontal axis indicates the gas flow rate while the injection rate of aqueous solution *p*-chlorophenol was kept at a constant value of 10 μL min^{-1}. Though in-

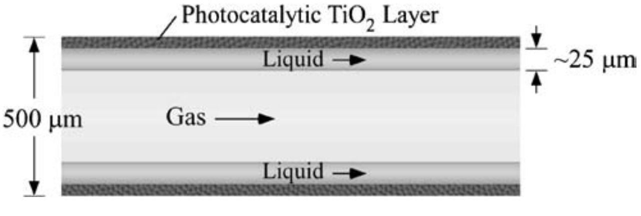

Figure 1. Schematic view of gas–liquid–solid annular.

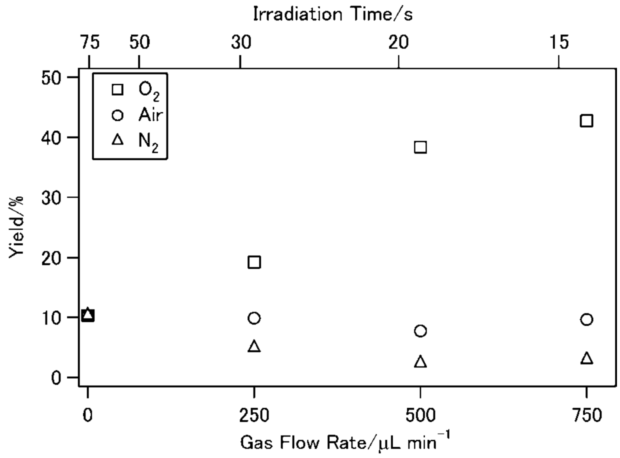

Figure 2. Photocatalytic oxidation of *p*-chlorophenol (1.0 mM) in aqueous solution under gas–liquid–solid multiphase flow conditions.

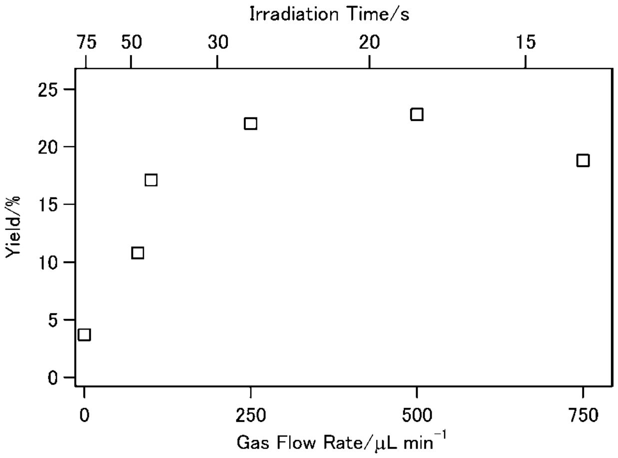

Figure 3. Photocatalytic oxidation of toluene (1.0 mM) in methanol under gas–liquid–solid multiphase flow conditions.

jection of air or nitrogen showed almost no or negative effect on photooxidation, the oxidation yield increased drastically by injection of oxygen gas under the annular flow conditions. The reaction yield increased up to 43% under the annular flow conditions while it was 10% at a residence time of 75 s without injection of oxygen gas.

Figure 3 indicates photocatalytic oxidation of toluene in methanol solution. The flow rate of oxygen varied from 0 to 750 mL min^{-1} while keeping the flow rate of the solution at 10 mL min^{-1}. The oxidation yield reached 23% under annular flow conditions while it was 3.7% without introducing oxygen gas.

It should be noted that the thickness of the liquid layer decreases and the liquid flows faster with increasing injection rate of the gas while maintaining the injection rate of the liquid at a constant value. The thickness and the flow rate of the liquid phase can be calculated by using the Levy kinetic energy exchange model.[14] At the gas flow rate of 500 µL min^{-1}, the thickness and irradiation time of the aqueous solution of *p*-chlorophenol were calculated to be 34 µm and 19 s, respectively, whereas these values are estimated to be 25 µm and 14 s at a gas flow rate of 750 µL min^{-1}. The degradation yield at a unit reaction time under the annular flow conditions was thus more than 20 times larger than that of homogeneous flow conditions without introducing gas phase.

It has been widely accepted that the illuminated specific surface area of a photocatalyst within a reactor is the most important design parameter for photocatalytic reactors.[15] The illuminated specific surface area per unit of liquid of a 500 × 500-µm^2 cross section microreactor is calculated to be 1.4×10^4 m^2 m^{-3} under homogeneous flow conditions. The value is much larger than the typical illuminated specific surface area of conventional photocatalytic batch reactors.[14] Under multiphase annular flow conditions, a thin layer of liquid phase is formed on the photocatalyst surface. The thickness of the liquid phase decreases and the illuminated specific surface area per unit of liquid increases with increasing gas injection rate. Further, under annular flow conditions, effective interaction between different phases is expected because of the extremely large interfacial area per unit volume and the short path required for molecular diffusion. Thus very efficient multiphase photocatalytic reactions might occur in the microreaction system.

In conclusion, we have developed a microreactor with an immobilized thin photocatalytic TiO_2 layer to examine photocatalytic oxidation of *p*-chlorophenol and toluene in multiphase flow conditions. By loading both gaseous and liquid samples, simultaneously into a microchannel with a thin photocatalyst layer therein, a gas–liquid–solid multiphase annular flow was generated, and reaction efficiency was greatly enhanced with decreasing thickness of the liquid layer. As the thickness of the liquid layer was decreased, contact area between different phases as well as illuminated specific surface area of photocatalyst per unit liquid volume substantially increased, while the path length required for molecular diffusion shortened. Thereby high reaction yield was obtained.

This work was supported by a Grant-in-Aid for Scientific Research (No. 20510115) from the Ministry of Education, Culture, Sports, Science and Technology of Japan and the New Energy and Industrial Technology Development Organization (NEDO), Project of Development of Microspace and Nanospace Reaction Environment Technology for Functional Materials.

References

1 V. Hessel, S. Hardt, H. Lowe, *Chemical Micro Process Engineering*, Wiley-VCH, Weinheim, **2004**.
2 T. Dietrich, *Principles and Applications of Chemical Microreactors*, Wiley-VCH, Weinheim, **2009**.
3 H. Nakamura, X. Li, H. Wang, M. Uehara, M. Miyazaki, H. Shimizu, H. Maeda, *Chem. Eng. J.* **2004**, *101*, 261.
4 R. Gorges, S. Meyer, G. Kreisel, *J. Photochem. Photobiol., A* **2004**, *167*, 95.
5 H. Lindstrom, R. Wootton, A. Iles, *AIChE J.* **2007**, *53*, 695.
6 Y. Matsushita, S. Kumada, K. Wakabayashi, K. Sakeda, T. Ichimura, *Chem. Lett.* **2006**, *35*, 410.
7 Y. Matsushita, N. Ohba, S. Kumada, T. Suzuki, T. Ichimura, *Catal. Commun.* **2007**, *8*, 2194.
8 Y. Matsushita, T. Ichimura, N. Ohba, S. Kumada, K. Sakeda, T. Suzuki, H. Tanibata, T. Murata, *Pure Appl. Chem.* **2007**, *79*, 1959.
9 Y. Matsushita, N. Ohba, S. Kumada, K. Sakeda, T. Suzuki, T. Ichimura, *Chem. Eng. J.* **2008**, *135*, S303.
10 Y. Matsushita, N. Ohba, T. Suzuki, T. Ichimura, *Catal. Today* **2008**, *132*, 153.
11 P. L. Mills, R. V. Chaudhari, *Catal. Today* **1997**, *37*, 367.
12 J. Kobayashi, Y. Mori, K. Okamoto, R. Akiyama, M. Ueno, T. Kitamori, S. Kobayashi, *Science* **2004**, *304*, 1305.
13 M. Czaplicka, *J. Hazard. Mater.* **2006**, *134*, 45, and references cited threin.
14 S. Levy, *Trans. ASME, Ser. C* **1960**, *82*, 113.
15 A. K. Ray, A. A. C. M. Beenackers, *AIChE J.* **1998**, *44*, 477.